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# Pressure Dependence of the Elastic Constants and an Experimental Equation of State for $CaF_2$†

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The elastic constants of $CaF_2$ have been measured under hydrostatic pressure to 4 kbar and at temperatures of 77.35, 194.5, 273.15, and 295.5°K. The ultrasonic data are analyzed according to the self-consistent method suggested by Cook. The result gives the adiabatic as well as the isothermal elastic constants directly as a function of pressure. From the pressure derivatives of the bulk modulus, we extrapolate the isotherms according to the Murnagham equation of state. The effective Debye temperature and Grüneisen constants have been calculated also as a function of pressure and temperature. While the Debye temperature at 4.2°K agrees well with other experiments, the Grüneisen constants calculated from the pressure derivatives of the elastic constants differ significantly from the macroscopic values. The reason is discussed. Our data are insufficient to resolve the discrepancy between the $\gamma$ calculated by Ganesan and Srinivasan and the $\gamma$ calculated from Batchelder and Simmons's experiment. Further experiments at low temperatures are needed.

## I. INTRODUCTION

THE study of anharmonic effects of crystal lattices[1] is important in understanding the temperature and pressure dependence of the physical properties of solids. This basic problem of lattice dynamics is approached generally by proposing an atomic model from which the phonon spectrum and dispersion curves can be calculated. Thermodynamic properties such as specific heat, thermal expansion, and elastic constants provide some measure of the average of the phonon spectrum. They can be useful as guidelines in restricting the lattice model. Elastic constants are particularly useful since they measure directly the long-wave portion of the dispersion curves. For $CaF_2$, the thermal expansivity,[2] the specific heat, and the elastic constants[3] have been carefully measured as a function of temperature. Part of this paper will report on the result of the measurement of the elastic constants as a function of pressure.

To measure the pressure dependence of the elastic constants, one faces the difficulty of knowing the length of sample at pressure and the conversion factor between the adiabatic and the isothermal elastic constants under pressure. We have solved these problems by using a self-consistent integration method suggested by Cook[4] in analyzing the ultrasonic data. The result yields the adiabatic as well as the isothermal elastic constants directly as a function of pressure.

Another part of this paper will show the application of elastic constants in evaluating some related thermodynamic properties of $CaF_2$. The equation of state can be easily obtained by integrating the bulk modulus. The Grüneisen constant is calculated from the Grüneisen formula and from the pressure derivatives of the elastic constants. The effective Debye temperature is also calculated.

## II. MEASUREMENT OF ELASTIC CONSTANTS

The technique and apparatus of measuring elastic constants[5] are well developed. Here we will describe the experiments briefly but discuss the sources of experimental error in some detail.

We use the phase-comparison method[6] to measure the transit time of an ultrasonic pulse travelling along certain directions in a single crystal. The $CaF_2$ single crystal of size $\frac{1}{2}$ in. cube and $\frac{1}{2}$ in.$\times\frac{1}{2}$ in.$\times 1$ in. are furnished by the Harshaw Chemical Company. To facilitate the data analysis by Cook's method, three single crystals are measured simultaneously; this also gives the necessary combination to determine the three elastic constants. The pressure vessel was designed by Martinson[7] for his Na work. Measurements were made at room temperature, ice point, dry-ice point, and liquid-$N_2$ point under hydrostatic pressure generated by a gas pressure system. We use glycerine as the bonding material for the 10 mc/sec quartz transducer at temperatures below 200°K and Nonaq grease at temperatures above 200°K.

The main sources of error in elastic-constant measurement are:

(1) The precision of measuring the sample length and of making the two opposite surfaces parallel. A supermicrometer can measure to $10^{-4}$ in. and it is not difficult to measure length to better than $10^{-5}$ in. But to prepare two faces parallel to one part in $10^4$ is another matter; this depends on the sample and the method of polishing. A careful mechanical polish of $CaF_2$ samples

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† Work supported by the U. S. Atomic Energy Commission.

[1] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 12.

[2] D. N. Batchelder and R. O. Simmons, J. Chem. Phys. 41, 2324 (1964).

[3] D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).

[4] R. K. Cook, J. Acoust. Soc. Am. 29, 445 (1957).

[5] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 213.

[6] A. D. Colvin, M.S. thesis, Rensselaer Polytechnic Institute, New York, 1959 (unpublished).

[7] R. H. Martinson, Ph.D. thesis, Cornell University, 1966 (unpublished).

**Table I.** Values of elastic constants and errors of measurement for $CaF_2$ at 1 atm and 77.35°K. The most probable values for the elastic constants are:

$$C_{11}{}^S=(17.1028\pm0.0037)\times10^{11}\ \mathrm{dyn/cm^2},$$
$$C_{12}{}^S=(4.6557\pm0.0132)\times10^{11}\ \mathrm{dyn/cm^2},$$
$$C_{44}{}^S=(3.6085\pm0.0052)\times10^{11}\ \mathrm{dyn/cm^2}.$$

| Crystal | Direction of wave motion | Direction of particle motion | Elastic constant measured | $\rho v^2$ ($10^{11}$ dyn/cm$^2$) | Error (%) |
|---|---|---|---|---|---|
| *A* | [100] | [100]*L* | $C_{11}{}^S$ | 17.0972 | 0.032 |
| | [100] | ⊥[100]*S* | $C_{44}{}^S$ | 3.6085 | ~0 |
| | [110] | [110]*L* | $\frac{1}{2}(C_{11}{}^S+C_{12}{}^S+2C_{44}{}^S)$ | 14.4892 | 0.010 |
| *B* | [110] | [110]*L* | $\frac{1}{2}(C_{11}{}^S+C_{12}{}^S+2C_{44}{}^S)$ | 14.4862 | 0.029 |
| | [110] | [001]*S* | $C_{44}{}^S$ | 3.5612 | 1.31 |
| | [110] | $[1\bar{1}0]$*S* | $\frac{1}{2}(C_{11}{}^S-C_{12}{}^S)$ | 0.6227 | 0.056 |
| *C* | [100] | [100]*L* | $C_{11}{}^S$ | 17.1083 | 0.032 |
| *D* | [111] | ⊥[111]*S* | $\frac{1}{3}(C_{11}{}^S-C_{12}{}^S+C_{44}{}^S)$ | 5.3530 | 0.021 |

fixed in a doughnut-shape mold with finely ground surfaces can produce surfaces parallel to one part in $10^4$. This puts an upper limit on the accuracy of measuring absolute values of elastic constants.

(2) The orientation of the crystal and the transducer. In our experiment the crystals are oriented by a Bragg diffractometer which gives an orientation accurate to less than 5/100 of a degree. There is no orientational error of the transducer for the longitudinal waves. However, to complete the measurement of the three elastic constants, at least one transverse wave is required. For certain transverse waves, the misorientation of the transducer can introduce the most significant error in the measurement. Waterman[8] has studied this problem carefully and has found that the error in sound-velocity measurement is roughly equal to the square of the misorientation measured in radians. Therefore, a misorientation of 2° will give an error of 1 part in $10^3$ for velocity and 2 parts in $10^3$ for the elastic constant. It is easy to introduce a 2° misorientation of the transducer during the experiment; the error then becomes serious. Fortunately, it is possible to eliminate this error by taking advantage of the degeneracy of the transverse waves along the [100] and [111] directions. We have used shear waves, always along one of these two directions, to eliminate the error in orienting the transducers.

(3) Correction for the phase shift in the bond. For thin bonds, the transit time $\tau$ can be expressed as[9]

$$2\tau=(n+\tfrac{1}{2})/f_n+k(1/f_n-1/f_0)\,, \tag{1}$$

where $n$ is the number of waves in the crystal, $f_0$ is the resonance frequency of the transducer, $f_n$ is the destructive-interference frequency of the $n$th mode, and $k$ is the ratio of the acoustic impedances of the crystal and the transducer. Here the error is due to the ambiguity of determining $n$, the validity of the thin-bond approximation and of knowing the resonance frequency of the transducer as a function of pressure and temperature. The first two problems can be solved by taking a sequence of the null frequencies and then by interpolating to find the transit time at the resonance frequency. McSkimin and Andreatch[10] have measured the pressure and temperature dependence of the quartz resonance frequency. However, it is difficult to measure precisely the resonance frequency of the transducer because of the coupling to the bond and the crystal. The total error is estimated to be about 1 part in $10^4$.

(4) Pressure and temperature measurement. The temperature measurement is not very critical in elastic-constant measurements especially at low temperatures. The pressure measurement is considered to be the most important error in the pressure derivatives. We use a Guildline potentiometer to measure the resistance change of the Manganin gauge under pressure. The potentiometer has a sensitivity of 1 part in $10^6$ and is considered to be sufficient for a pressure change of 1 bar. The problem here is the calibration of the Manganin gauge and occasionally the existence of gas leaks from the pressure vessel. The reproducibility of the pressure derivatives in our work on $CaF_2$ is about 2%.

We have made some measurements at 77.35°K and 1 atm to check the source of errors in our experiment. The result is summarized in Table I.

## III. ANALYSIS OF ULTRASONIC DATA

The adiabatic elastic constant, or a combination of elastic constants is given by

$$\begin{aligned} C^S(P)&=\rho(l/\tau)^2,\\ &=\rho_0(l_0/\tau)^2S(P)\,, \end{aligned} \tag{2}$$

where $\rho_0$ and $\rho$ are the densities at $P=0$ and $P=P$, respectively, and $S(P)=l_0/l$ is the ratio of the initial

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[8] P. C. Waterman, Phys. Rev. **113**, 1240 (1959).

[9] J. William and J. Lamb, J. Acoust. Soc. Am. **30**, 308 (1958).

[10] H. J. McSkimin and P. Andreatch, J. Acoust. Soc. Am. **34**, 609 (1962).

TABLE II. The pressure dependence of the isothermal elastic constants of $CaF_2$.

| $p$ | $\rho$ | $C_{11}^T$ | $C_{12}^T$ | $C_{44}^T$ | $\Delta$ |
|---|---|---|---|---|---|
| | | (a) 295.5°K | | | |
| 0.001 | 3.1795 | 16.057 | 4.344 | 3.380 | 2.719 |
| 0.264 | 3.1805 | 16.108 | 4.332 | 3.387 | 2.723 |
| 0.582 | 3.1817 | 16.113 | 4.363 | 3.391 | 2.729 |
| 0.950 | 3.1832 | 16.125 | 4.393 | 3.396 | 2.736 |
| 1.269 | 3.1844 | 16.145 | 4.413 | 3.400 | 2.742 |
| 1.669 | 3.1859 | 16.166 | 4.435 | 3.405 | 2.748 |
| 2.126 | 3.1876 | 16.200 | 4.460 | 3.411 | 2.756 |
| 2.629 | 3.1895 | 16.233 | 4.486 | 3.417 | 2.764 |
| 3.139 | 3.1915 | 16.272 | 4.514 | 3.424 | 2.773 |
| | | (b) 273.15°K | | | |
| 0.001 | 3.1835 | 16.163 | 4.382 | 3.409 | 2.580 |
| 0.265 | 3.1845 | 16.197 | 4.371 | 3.410 | 2.586 |
| 0.578 | 3.1857 | 16.198 | 4.407 | 3.415 | 2.592 |
| 0.911 | 3.1870 | 16.208 | 4.434 | 3.419 | 2.598 |
| 1.281 | 3.1884 | 16.231 | 4.456 | 3.423 | 2.604 |
| 1.741 | 3.1901 | 16.265 | 4.477 | 3.429 | 2.610 |
| 2.026 | 3.1912 | 16.282 | 4.493 | 3.433 | 2.615 |
| 2.520 | 3.1931 | 16.317 | 4.515 | 3.439 | 2.622 |
| 3.030 | 3.1950 | 16.352 | 4.540 | 3.446 | 2.629 |
| 3.505 | 3.1968 | 16.383 | 4.565 | 3.452 | 2.636 |
| 4.028 | 3.1988 | 16.419 | 4.593 | 3.458 | 2.644 |
| | | (c) 194.5°K | | | |
| 0.001 | 3.1963 | 16.582 | 4.486 | 3.500 | 1.549 |
| 0.241 | 3.1972 | 16.597 | 4.497 | 3.504 | 1.551 |
| 0.574 | 3.1984 | 16.617 | 4.509 | 3.508 | 1.553 |
| 0.924 | 3.1998 | 16.638 | 4.522 | 3.512 | 1.556 |
| 1.273 | 3.2011 | 16.659 | 4.535 | 3.516 | 1.558 |
| 1.615 | 3.2023 | 16.680 | 4.548 | 3.520 | 1.560 |
| 2.129 | 3.2042 | 16.711 | 4.567 | 3.527 | 1.564 |
| 2.677 | 3.2063 | 16.742 | 4.590 | 3.533 | 1.567 |
| 3.189 | 3.2082 | 16.771 | 4.611 | 3.539 | 1.571 |
| 3.732 | 3.2102 | 16.803 | 4.631 | 3.546 | 1.574 |
| 4.164 | 3.2118 | 16.827 | 4.647 | 3.551 | 1.577 |
| | | (d) 77.35°K | | | |
| 0.001 | 3.2085 | 17.064 | 4.648 | 3.609 | 1.820 |
| 0.158 | 3.2091 | 17.078 | 4.653 | 3.610 | 1.821 |
| 0.272 | 3.2095 | 17.081 | 4.655 | 3.610 | 1.821 |
| 1.072 | 3.2124 | 17.130 | 4.691 | 3.621 | 1.828 |
| 1.538 | 3.2141 | 17.159 | 4.711 | 3.627 | 1.832 |
| 1.848 | 3.2152 | 17.178 | 4.724 | 3.630 | 1.834 |
| 2.381 | 3.2171 | 17.209 | 4.748 | 3.636 | 1.839 |
| 2.936 | 3.2191 | 17.246 | 4.766 | 3.642 | 1.842 |
| 3.409 | 3.2209 | 17.273 | 4.789 | 3.648 | 1.847 |

[a] Units: $p$, kbar; $\rho$, g/cm$^3$; $C_{11}^T$, $C_{12}^T$, $C_{44}^T$, $10^{11}$ dyn/cm$^2$; $\Delta$, %.

sample length to the length at $P$ atmospheres. Cook's method provides a self-consistent way of calculating $S$ as a function of pressure. Since

$$\tfrac{1}{3}S(dP/dS)=\tfrac{1}{3}(C_{11}^T+2C_{12}^T),$$
$$=(C_{11}^S+2C_{12}^S)/3(1+\Delta),$$

therefore,

$$S(P)=1+\frac{1}{3\rho_0 l_0^2}\int_0^P(1+\Delta)\tau_B^2 dP. \tag{3}$$

Here we use the superscript $T$ and $S$ to designate the isothermal and adiabatic elastic constants and $\Delta=\beta^2TB^S/\rho C_P$, the conversion factor between the isothermal and adiabatic constants; $\Delta$ is, of course, a function of pressure itself.

In our experiment, in order to eliminate the error from misorientation of transducers, we work with the longitudinal waves along [100] and [110] directions and the transverse waves along [100] and [111] directions. The corresponding elastic constants have been listed in Table I. A combination of three of these waves will give $\tau_B$. Equation (3) is solved by iterated integration; since $\Delta$ and $S$ are functions of pressure, the adiabatic and the isothermal elastic constants can be easily calculated. The pressure derivatives are evaluated by the standard least-squares method.

We have made two pressure runs at each of the fixed temperatures 295, 273.15, 194.5, and 77.35°K. The results from the Cook's analysis are tabulated in Table II for one of the runs. The conversion factor $\Delta$ is also listed to facilitate the calculation of the adiabatic elastic constants. The average values of the pressure derivatives are collected in Table III. It is also tempting to calculate the second pressure derivatives; however, due to the hardness of $CaF_2$ and the maximum pressure employed, namely, 5 kbar, their values should be considered as only an order-of-magnitude estimate. We show the values for the bulk modulus in Table IV.

## IV. EQUATION OF STATE

If we write the pressure dependence of the isothermal bulk modulus as a Maclauren expansion

$$B^T=-V\partial P/\partial V|_T=B_0^T+B_0^{T\prime}P+\tfrac{1}{2}B_0^{T\prime\prime}P^2, \tag{4}$$

then the isotherms can be obtained by integration. In fact, a linear expansion of $B^T$ in $P$ will give the so-called Murnaghan equation of state[11]:

$$V/V_0=[1+(B_0^{T\prime}/B_0^T)P]^{-1/B_0^{\prime}}. \tag{5}$$

For $CaF_2$ we expect Eq. (5) to hold reasonably well at pressure as high as 200 kbar since the contribution of the $\tfrac{1}{2}B_0^{T\prime\prime}P^2$ is only $\tfrac{1}{2}\%$ at 100 kbar and 2% at 200 kbar. Two isotherms at 77.35 and 194.5°K are plotted in Fig. 1. There is no static-pressure measurement nor shock-wave experiment available for comparison.

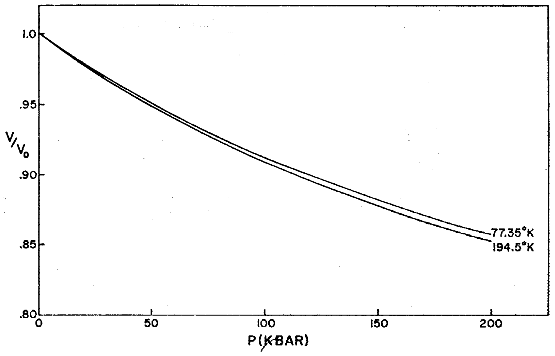

FIG. 1. The isotherms of $CaF_2$ at 77.35 and 194.5°K calculated from Murnagham's equation of state.

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[11] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

TABLE III. The pressure derivatives of the elastic constants of $CaF_2$. All elastic constants are in units of $10^{11}$ dyn/cm$^2$ and their pressure derivatives are dimensionless.

| | 295.5°K | 273.15°K | 194.5°K | 77.35°K |
|---|---|---|---|---|
| $C_{11}{}^{T}(0)$ | 16.071±0.006 | 16.161±0.005 | 16.583±0.001 | 17.065±0.001 |
| $C_{11}{}^{T\prime}$ | 6.20 ±0.35 | 6.24 ±0.20 | 5.89 ±0.03 | 6.09 ±0.04 |
| $C_{11}{}^{S}(0)$ | 16.507±0.006 | 16.578±0.005 | 16.840±0.001 | 17.096±0.001 |
| $C_{11}{}^{S\prime}$ | 6.62 ±0.37 | 6.65 ±0.21 | 6.11 ±0.03 | 6.12 ±0.04 |
| $C_{12}{}^{T}(0)$ | 4.334±0.005 | 4.377±0.004 | 4.487±0.001 | 4.646±0.001 |
| $C_{12}{}^{T\prime}$ | 5.85 ±0.27 | 5.43 ±0.20 | 3.86 ±0.02 | 4.16 ±0.05 |
| $C_{12}{}^{S}$ | 4.451±0.005 | 4.490±0.005 | 4.556±0.001 | 4.655±0.001 |
| $C_{12}{}^{S\prime}$ | 6.08 ±0.28 | 5.64 ±0.21 | 3.96 ±0.02 | 4.17 ±0.06 |
| $C_{44}(0)$[a] | 3.383±0.001 | 3.407±0.001 | 3.501±0.001 | 3.608±0.001 |
| $C_{44}{}'$ | 1.33 ±0.04 | 1.26 ±0.01 | 1.21 ±0.01 | 1.17 ±0.02 |

[a] The isothermal and the adiabatic values for $C_{44}$ are the same.

## V. EFFECTIVE DEBYE TEMPERATURE AND GRÜNEISEN CONSTANT

At 0°K the Debye temperature is given by

$$\Theta_D=\frac{h}{k}\left(\frac{3q}{4\pi}\frac{N\rho}{M}\right)^{1/3}v_m\,, \tag{6a}$$

where $q$ equals the number of atoms in the molecule (3 for $CaF_2$), $N/M$ is the number of atoms per gram, and $v_m$ is the average sound velocity which can be calculated by the following spatial integral[12]:

$$v_m=\left[\frac{1}{3}\sum_{i=1}^{3}\int\frac{1}{v_i^3}\frac{d\Omega}{4\pi}\right]^{-1/3}. \tag{6b}$$

For temperatures above 0°K, Eq. (6a) gives the effective Debye temperature. We evaluate the effective Debye temperature as a function of temperature and pressure. To check the agreement between the Debye temperatures calculated from elastic constants and from specific-heat data near 0°K at which the two Debye temperatures should be equal, we have also measured the elastic constants at 4.2°K. The results are

$$C_{11}{}^{T}=17.124\times10^{11}\text{ dyn/cm}^2,$$
$$C_{12}{}^{T}=4.675\times10^{11}\text{ dyn/cm}^2,$$
$$C_{44}{}^{T}=3.624\times10^{11}\text{ dyn/cm}^2.$$

The corresponding Debye temperature is 519.4°K, while the calorimetric value is 508±5°K.

TABLE IV. The pressure derivatives of the isothermal bulk modulus of $CaF_2$.

| $T$°K | $B_0{}^{T}$ ($10^{11}$ dyn/cm$^2$) | $B_0{}^{T\prime}$ | $B_0{}^{T\prime\prime}$ ($10^{-10}$ cm$^2$/dyn) |
|---|---|---|---|
| 295.5 | 8.254±0.002 | 6.08±0.27 | −0.8±1.7 |
| 273.15 | 8.304±0.002 | 5.91±0.26 | −1 ±1.3 |
| 194.5 | 8.518±0.001 | 4.60±0.06 | −0.3±0.3 |
| 77.35 | 8.800±0.001 | 5.48±0.16 | −0.2±1 |

The Grüneisen constant is defined as

$$\gamma=\sum_i\gamma_iC_{Vi}/\sum_iC_{Vi}\,, \tag{7a}$$

with the mode $\gamma_i$ defined as

$$\gamma_i=\partial\ln\omega_i/\partial\ln V\,, \tag{7b}$$

where $C_{Vi}$ is the contribution to the specific heat $C_V$ from the $i$th phonon of frequency $\omega_i$. It is impossible to calculate $\gamma$ without a proper atomic model and detailed calculations in lattice dynamics. Generally an approximation is used to evaluate $\gamma$. Grüneisen assumes that all $\gamma_i$ are equal; then $\gamma$, called the macroscopic $\gamma_m$, can be expressed as

$$\gamma_m=\beta VB^S/C_p=\beta VB^T/C_V\,. \tag{8}$$

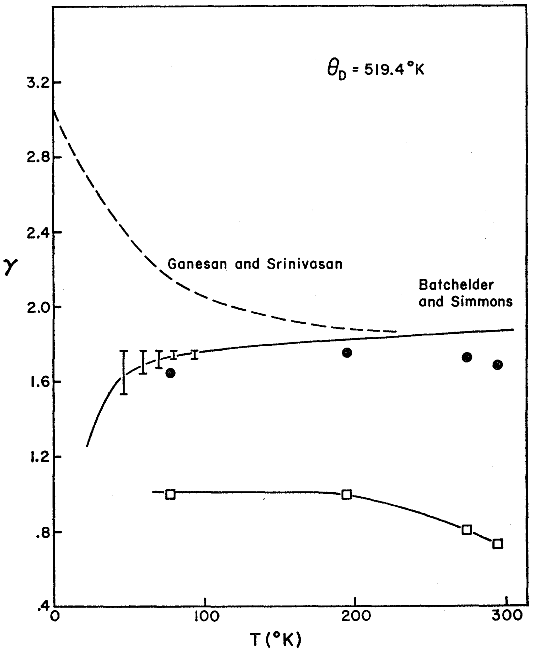

FIG. 2. Temperature variations of the Grüneisen constant of $CaF_2$. Circles are the macroscopic $\gamma$ values calculated from Eq. (8); squares represent the $\gamma$ values calculated from the pressure derivatives of the elastic constants. The Batchelder and Simmon's values are obtained from their thermal-expansion measurements and the Ganesan and Srinivasan values are calculated according to a rigid-ion model.

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[12] G. A. Alers, *Physical Acoustics* (Academic Press Inc., New York, 1965), Vol. III, Part B.

TABLE V. Effective Debye temperature and Grüneisen constants of $CaF_2$.

| $T$(°K) | $P$(kbar) | $\theta_0$(°K) | $\gamma_0$ | $\gamma_m$ |
|---|---|---|---|---|
| 4.2 | 0 | 519.4 | | |
| 77.35 | 0 | 518.7 | 0.994 | 1.650 |
| | 1.072 | | | 1.665 |
| | 1.848 | | | 1.675 |
| | 2.936 | | | 1.689 |
| | 3.409 | | | 1.695 |
| 194.5 | 0 | 512.9 | 1.026 | 1.736 |
| | 0.924 | | | 1.745 |
| | 2.129 | | | 1.757 |
| | 3.189 | | | 1.768 |
| | 4.164 | | | 1.778 |
| 273.15 | 0 | 507.5 | 0.798 | 1.723 |
| | 0.911 | | | 1.733 |
| | 2.026 | | | 1.745 |
| | 3.030 | | | 1.756 |
| | 4.028 | | | 1.768 |
| 295.5 | 0 | 506.2 | 0.727 | 1.679 |
| | 0.950 | | | 1.689 |
| | 1.669 | | | 1.697 |
| | 2.629 | | | 1.708 |
| | 3.139 | | | 1.713 |

At low temperatures, only the long-wave phonons contribute to the specific heat; Eq. (7a) becomes

$$\gamma_0 = \int\left[\sum_i \frac{\gamma_i}{v_i^3}\right]d\Omega \bigg/ \int\left[\sum \frac{1}{v_i^3}\right]d\Omega, \tag{9a}$$

where the integrations are carried out over all solid angles. The mode $\gamma_i$ are related to the pressure derivatives in the following manner:

$$\gamma_i = -\tfrac{1}{6} + (B^T/2C_i^T)dC_i^T/dP. \tag{9b}$$

Equations (9a) and (9b) should be valid in the temperature range where $C_V \propto T^3$. It is tempting, as is often done, to calculate $\gamma$ at high temperatures ($T > \Theta_D$) by taking out the $1/v_i^3$ weighing factor since all phonons are excited. However, Eq. (9b) becomes insufficient to account for all mode $\gamma_i$'s; thus the pressure derivatives of elastic constants do not give enough information in evaluating $\gamma$ at high temperatures.

To calculate the two spatial integrals in Eqs. (6b) and (9a) properly, one must solve $\gamma_i$ and $v_i$ along arbitrary directions in space and then integrate them numerically. A computer program was employed for these calculations. The results together with the $\gamma_m$ values calculated as a function of pressure are summarized in Table V.

## VI. DISCUSSION

It is clear that Cook's method provides a proper analysis of the ultrasonic data under hydrostatic pressure. Its application is straightforward and the self-consistent integration can be carried out easily with the aid of a computer. A complication in the experiment is that at least two sound velocities must be measured simultaneously as a function of pressure in order to obtain the transit time corresponding to the bulk modulus.

In Table VI we compare our elastic constants of $CaF_2$ at room temperature with those obtained by other authors. There is no clear indication that the values measured in other experiments are isothermal or adiabatic. Nevertheless, the comparison is made with our adiabatic values. The agreement in $C_{11}^S$ and $C_{44}^S$ is excellent, while the discrepancy in $C_{12}^S$ could mainly be due to the misorientation of the transducer. There are no experimental pressure derivatives of elastic constants of $CaF_2$ available for comparison.

We have shown some applications of the elastic constants in calculating the thermodynamic properties of $CaF_2$ such as the equation of state, the effective Debye temperature, and the Grüneisen constants. It is also possible to develop a phenomenological atomic model, for instance, the simple Born von Karman model, by adjusting the model parameters according to the elastic constants, and to proceed to calculate the atomic properties of the solid.

Anderson[13] found that for most substances the Murnaghan equation of state describes the compression of the solid better than a polynomial expansion of $\Delta V/V_0$ in terms of pressure. For $CaF_2$, since the contribution of the second pressure derivative is small, the isotherms determined from elastic-constant data at low temperatures should be quite satisfactory for pressures as high as 200 kbar.

The Debye temperature at 4.2°K is calculated to be 519.4±0.1°K. This value is in good agreement with the following ones due to Huffman and Norwood[3]:

$$\Theta_0 \text{ (elastic constants)} = (513.6\pm2.5)°\text{K},$$
$$\Theta_0 \text{ (specific heat)} \quad = (508\pm5)°\text{K}.$$

The temperature variation of the Grüneisen constant is very interesting. Batchelder and Simmons[2] found that the $\gamma$ calculated from their thermal expansion measurement [see Fig. 2] decreases with temperature; this contradicts the Ganesan and Srinvasan's[14]

TABLE VI. Comparison of elastic-constant values of $CaF_2$ at room temperature (units of $10^{11}$ dyn/cm$^2$).

| | $C_{11}^S$ | $C_{12}^S$ | $C_{44}^S$ |
|---|---|---|---|
| Voigt[a] | 16.4 | 4.47 | 3.38 |
| Bhagavanatham[b] | 16.44 | 5.02 | 3.47 |
| Huffman and Norwood[c] | 16.4 | 5.3 | 3.370 |
| Haussühl[d] | 16.357 | 4.401 | 3.392 |
| Srinivasan[e] (theoretical) | 16.8 | 4.8 | 4.0 |
| Present work | 16.494 | 4.462 | 3.380 |

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[d] S. Hanssühl, Phys. Status Solidi **3**, 1072 (1963).
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prediction based on a solid-sphere model. Since it is very difficult to measure the thermal expansion at low temperatures, the low-temperature $\gamma$ determined from the Grüneisen formula is no longer reliable. Therefore, it was suggested that an independent $\gamma$ determined from the low-temperature pressure derivatives of elastic constants [see Eq. (9a) and (9b)] can resolve this problem. However, as seen from Table V, the $\gamma$ calculated from these two formulas are not equal since the Grüneisen assumption does not apply for $CaF_2$; for instance, at 77.35°K the average mode $\gamma$ of the longitudinal wave is 1.66 and for the transverse waves, the $\gamma$ are 0.81 and 0.98. The $\gamma_0$ calculated from the pressure derivatives of elastic constants should be reasonably accurate at 78°K and below because of the high Debye temperature of $CaF_2$. Judging from our result, there is little change of $\gamma$ above 78°K. The value of $\gamma$ for temperatures below 78°K cannot be known until more measurements at low temperatures are completed. We plan to continue this experiment to low-temperature regions in the near future.

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# Electron Paramagnetic Resonance and Spectroscopic Study of $LaCl_3$:$Eu^{2+}$ and Associated Color Centers*†

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The electron-paramagnetic-resonance (EPR) spectrum of $LaCl_3$:$Eu^{2+}$ was observed to obtain the ground-state splitting of $Eu^{2+}$ in sites of $C_{3h}$ symmetry. A good fit to the observed energy levels in the ground manifold of $Eu^{2+}$ was provided by the parameters $b_2{}^0=427.20\times10^{-4}$ cm$^{-1}$, $b_4{}^0=5.48\times10^{-4}$ cm$^{-1}$, $b_6{}^0=-0.045\times10^{-4}$ cm$^{-1}$, $b_6{}^6=2.97\times10^{-4}$ cm$^{-1}$, $g_\parallel=1.9924$, and $g_\perp=1.9927$. The shift in $b_2{}^0$ from room temperature to 4.2°K was less than 5%. EPR spectra which could be attributed to europium ions in at least one other inequivalent site were observed but not analyzed in detail. The color centers produced in $LaCl_3$:$Eu^{2+}$ by ultraviolet radiation appeared to be due to electrons removed by the radiation from $Eu^{2+}$ ions, which were then trapped at certain crystal defects. The $Eu^{2+}$ donors were shown to reside in the normal $C_{3h}$ rare-earth sites, and the polarization of the color-center absorption spectrum indicated that the color-center defects had relatively high symmetry. If the color-center defects were due to anion vacancies such as one finds for certain color centers in alkali halide crystals, then the defect was probably a cluster of more than one chlorine vacancy.

## I. INTRODUCTION

THIS paper presents the results of an optical and electron-paramagnetic-resonance (EPR) study of $LaCl_3$:$Eu^{2+}$. The two significant features are the large splitting of the $^8S_{7/2}$ ground state and the polarized color-center absorption bands which are easily produced by ultraviolet radiation. A comparison of the splitting of the $^8S_{7/2}$ state of $Eu^{2+}$ and $Gd^{3+}$ is of interest since the explanation of this splitting is not yet complete.[1,2] Using EPR, the ground-state splitting of $Eu^{2+}$ in $C_{3h}$ sites in $LaCl_3$ has been determined to be approximately 50 times that of $Gd^{3+}$. This may indicate that configuration interaction is important in the splitting of the ground states of $Gd^{3+}$ and $Eu^{2+}$.

It has been previously reported[3,4] that color centers are formed in $LaCl_3$ containing divalent europium. [One of the striking features of this phenomenon is the relative ease with which these crystals can be colored and bleached. A modest amount of color can be induced in these crystals by subjecting them to the unfiltered ultraviolet radiation from a low-pressure mercury-discharge tube (pen lamp) for a few minutes at room temperature. Bleaching can be accomplished by heating the colored crystal to temperatures as low as 100°C.

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